

Volatile Flavor Components of Deep Fat-Fried Soybeans

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The volatile flavor components of deep fat-fried soybeans have been isolated, fractionated, and identified with the techniques of gas chromatography and mass spectrometry. Several carbonyls,

aromatic compounds, pyrazine, and pyrrole derivatives have been identified. Their origins and possible contributions to the characteristic "peanut butter-like" aroma of deep fat-fried soybeans are discussed.

Soybeans possess "green or beany" flavor which affects their use as food for human consumption. One of the processing techniques for altering the objectionable odor to desirable aroma is "oil roasting" or "deep fat frying" (Badenhop *et al.*, 1968). During deep fat frying, soybeans are completely submerged in a heated edible oil and subjected to a rapid dehydration followed by a partial pyrolysis and chemical interactions among soybean constituents. Deep fat-fried soybeans have a pleasant odor which is the characteristic of roasted nut or peanut butter-like aroma. This paper deals with the isolation and identification of some volatile components from deep fat-fried soybeans.

MATERIALS AND METHODS

Sample Preparation. Whole soybeans, variety Harasoy 63, were soaked in 70° C water for 2 hr and dehulled by passing them through a Quaker City mill (Model F No. 4) which had the grinding plates spaced far enough apart to loosen the hulls from the beans. After the hulls were loosened from the cotyledons, they were separated by a water flotation procedure. About 300 g of the cotyledons were then deep-fat fried in corn oil at 190° C for 4.5 min.

Two parts of the fried soybean were ground with 10 parts of distilled water in a Model CB-5 Waring Blender for 2 min on low speed. Open system steam distillation, *i.e.*, distillation with the introduction of extraneous steam, was carried out at atmospheric pressure until approximately 1 l. of distillate was collected. Sample was maintained at 95° ± 2° C throughout the distillation. The aroma of distillate possessed the characteristic flavor of the starting material.

The volatiles were extracted from the distillate with approximately 150 ml redistilled CS₂ in a continuous liquid-liquid extractor at the recycle rate of 25 to 30 ml per min.

Gas Chromatography. Components of the CS₂ extract were fractionated with a Varian Aerograph Model 1520B gas chromatograph on a 10-ft × 1/4-in. o.d. aluminum column packed with 20% SE-30 on 60-70 mesh Anakrom AB at a helium flow rate of 60 ml per min. The temperature was programmed from 70 to 275° C at 1° C per min. Eighteen

fractions were collected in 16-in. × 2-mm i.d. glass tubes with dry ice coolants. Each fraction was rechromatographed on a 10-ft × 1/4-in. o.d. aluminum column packed with 25% Carbowax 20M on 60-70 mesh Anakrom AB at a helium flow rate of 60 ml/min. The temperature was programmed from 50° to 250° C at 1° C/min. The subfractions were rechromatographed on a 10-ft × 1/8-in. o.d. stainless steel column packed with 25% Carbowax on 60-70 mesh Anakrom AB at a helium flow rate of 30 ml/min with temperature programming from 50° to 250° C at 1° C/min for relative retention time data against a series of ethyl ester standards.

Gas Chromatography-Mass Spectrometry. The subfractions were rechromatographed under conditions similar to those used for retention time data. The effluent was passed into a heated (200° C) helium separator (Watson and Biemann, 1964) interfaced at the inlet of a Model 12-101A Bendix Time-of-Flight mass spectrometer. The elution of compounds was observed through the use of a Bendix total output integrator and a Textronic Type 545B oscilloscope. The scan rate was set to give a 5-sec scan between *m/e* 40 and 150.

RESULTS AND DISCUSSION

The gas chromatographic separation of the total volatile distillate in the Carbowax 20M column is shown in Figure 1. Relative retention time indices (*I_R*) of both unknown and authentic compounds were calculated relative to a series of internal ethyl ester standards, where the carbon chain length of the acid function represents a whole number, *e.g.*, ethyl hexanoate = 6.00 (van den Dool and Kratz, 1963).

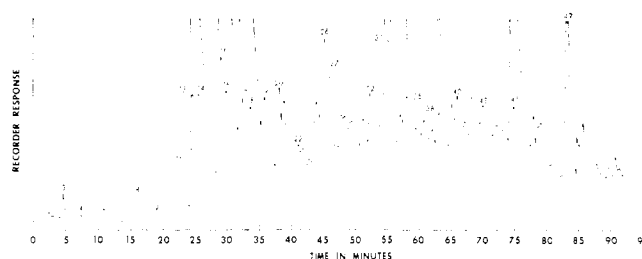


Figure 1. Gas chromatogram of the volatile components from deep fat-fried soybeans

Programmed at 2° C per min from 50° C to 250° C on a 10-ft × 1/4-in. o.d. Carbowax 20M column

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Table I. Identification of Compounds Found in the Volatile Flavor of Deep Fat-Fried (Oil Roasted) Soybeans

Peak No.	Compound	Size of Peaks ^a	I _E Relative Retention Time Indices		Mass Spectral Identification	Reference	Peak Identification Comment ^a
			Unknown	Authentic			
1	2-Methylpropanal	S	1.00	...	+	A	P
2	Acetone	S	1.00	...	+	A	P
3	Ethanol	S	2.43	2.34		A	T
4	2-Methyl-2-butanol	S	3.26	...	+	(Cornu and Massot, 1966)	P
5	2,3-Pentanedione	S	4.18	4.14	+	A	P
6	Dimethyldisulfide	S	4.08	4.00			T
	Hexanal	S	4.48	4.43	+	A	P
7	1-Penten-3-ol	S	4.92	5.04	+	(Bondarovich <i>et al.</i> , 1967a)	P
8	2-Heptanone	S	5.47	5.41	+	A	P
9	Pyrazine	S	5.91	...	+	(Bondarovich <i>et al.</i> , 1967b)	P
10	Pentanol	S	6.00	6.00	+	A	P
11	2-Methylpyrazine	S	6.30	6.55	+	A	P
12	2-Octanone	S	6.54	6.55	+	A	P
13	2,5-Dimethylpyrazine	M	6.84	6.60	+	A	P
14	2,3-Dimethylpyrazine	M	7.08	7.09	+	(Bondarovich <i>et al.</i> , 1967b)	P
15	2-Ethyl-5-methylpyrazine	M	7.56	7.54	+	(Bondarovich <i>et al.</i> , 1967b)	P
16	Trimethyl pyrazine	L	7.67	7.88	+	A	P
17	1-Octen-3-ol	VL	8.00	8.00	+	A	P
	2-Ethyl-3,6-dimethyl pyrazine	VL	8.03	...	+	(Bondarovich <i>et al.</i> , 1967b)	P
18	Furfural	M	8.25	8.32	+	A	P
19	2-Furfuryl methyl ketone	M	8.60	8.64	+	A	P
20	Benzaldehyde	S	8.91	8.82	+	A	P
22	5-Methyl furfural	S	9.41	9.44	+	A	P
26	Phenylacetaldehyde	S	10.02	10.14	+	(Bondarovich <i>et al.</i> , 1967a)	P
27	Furfuryl alcohol	S	10.00	10.00	+	(Cornu and Massot, 1966)	P
32	2,4-Decadienal	S	11.21	...	+	A	P
33	2,4-Decadienal	M	11.68	11.67	+	A	P
35	Guaiacol	M	12.19	12.34	+	A	P
38	Acetopyrrole	M	13.12	...	+	(Budzikiewicz <i>et al.</i> , 1967)	P
40	Pyrrrol-2-carboxaldehyde	S	13.61	...			T
43	1-Methylpyrrole-2-carboxaldehyde	S	14.36	...	+	(Stoll <i>et al.</i> , 1967)	P
45	4-Vinyl guaiacol	VL	15.31	15.61	+	A	P
49	2,3-Dihydrobenzofuran	L	17.12	...		(Stoll <i>et al.</i> , 1967)	T

^a P = positive; T = tentative; A = authentic compound; S = small; M = medium; L = large; VL = very large.

Relative quantities of the compounds were indicated by the sizes of chromatographic peaks as shown in Table I. A (+) symbol in the mass spectra column indicated mass spectral agreement with the reference mass spectra. Peak identifications were remarked as "positive" or "tentative" in the comment column of Table I.

Approximately 60 peaks were evidenced in the chromatogram (Figure 1). Many of these peaks consisted of two or more compounds and were separated by first collecting cuts on the nonpolar column and rechromatographing on the carbowax column. Many of the smaller components remained unidentified because of mass spectral sensitivity limitation combined with overlapping peaks and background, especially at the higher temperature region of glc.

Definite identification of 28 compounds was obtained, and four compounds were tentatively identified: 4-vinyl guaiacol, 2-ethyl-3,6-dimethylpyrazine, and 1-octen-3-ol were present in large quantities. Considerable amounts of 2,4-decadienal, guaiacol, and the derivatives of pyrazine, pyrrole, and furan were also present as notable constituents of deep fat-fried soybeans.

Large quantities of carbonyls and alcohols have been found in raw soybeans (Arai *et al.*, 1967; Fujimaki *et al.*, 1965; Mattick and Hand, 1969). The majority have been described as possessing undesirable odor which partially contributes to "raw" or "beany" flavor of soybean and its products. Except 2,4-decadienal and 1-octen-3-ol, only small amounts of

carbonyls and alcohols were found in the volatiles of deep fat-fried soybeans (Table I).

1-Octen-3-ol was likely to arise from soybean (Badenhop and Wilkens, 1969) and the decomposition of corn oil during deep fat frying (Krishnamurthy and Chang, 1967). Although a large amount of 1-octen-3-ol was found, its characteristic "mushroom-like" odor did not impair the pleasant aroma of deep fat-fried soybeans.

A large amount of 2,4-decadienal was found in peak 33 and a small amount in peak 32 (Figure 1). This compound had two different retention times in glc due to stereoconfiguration of the isomers (2t, 4c, and 2t, 4t) (Hoffman, 1961). The compound arose from the autoxidation of linoleic acid, a component of soybean oil, and the corn oil used for deep fat frying. 2,4-Decadienal is believed to impart a desirable deep fat flavor to a food (Mookherjee *et al.*, 1965).

Several aromatic compounds were identified. Small amounts of benzaldehyde were detected (peak 20). Its odor can be described as "almond-like." Benzaldehyde arose from soybean oil (Smouse and Chang, 1967) and the corn oil used for deep fat frying (Krishnamurthy and Chang, 1967).

Phenylacetaldehyde (peak 26) might be formed from the corn oil, but more likely is formed from the amino acid phenylalanine in the soybean by Strecker degradation during deep fat frying. Its aroma is described as "pleasant, floral." Phenylacetaldehyde has been reported to be one of the major volatile components in roasted peanuts (Mason *et al.*, 1966),

in potato chips (Deck, 1968), tea (Viani *et al.*, 1966; Bondarovich *et al.*, 1967a), roasted cocoa (van Praag *et al.*, 1968), coffee (Stoll *et al.*, 1967), rye crispbread (von Sydow and Anjou, 1969), etc.

A large amount of 4-vinyl guaiacol (peak 45), and guaiacol (peak 35) might be formed from the thermal degradation of ferulic acid (Fiddler *et al.*, 1967) which was reported to be one of the phenolic acids found in defatted soybean flour (Arai *et al.*, 1966). Neukom (1969) attributed the presence of small quantities of 4-vinylguaiacol in whiskey to the same decomposition reaction.

Considerable amounts of furfural, 2-furfuryl methyl ketone 5-methyl furfural, and furfuryl alcohol in the volatiles of deep fat-fried soybeans might also contribute to the aroma. These furan derivatives can arise from carbohydrates as shown by many model experiments by Hodge (1967).

Several pyrazine and pyrrole derivatives were identified. Large quantities and the typical odor of alkyl-substituted pyrazines suggest that they were responsible for the "nut-like" or "peanut-butter-like" aroma of deep fat-fried soybeans. Just as some aromatic and furan compounds are formed, these nitrogen compounds are derived from thermal reactions during the deep fat frying to 190° C. None of these compounds were found in raw soybeans or soy milk which was prepared under 100° C.

The pyrazine compounds have also been found in potato chips (Deck, 1968), coffee (Bondarovich *et al.*, 1967b; Goldman *et al.*, 1967), cocoa (Marion *et al.*, 1967; Rizzi, 1967; van Praag, 1968), peanuts (Newell *et al.*, 1967), rye crispbread (von Sydow and Anjou, 1969), etc. Newell *et al.* (1967) proposed a mechanism for the formation of pyrazine compounds from the interaction of amino acids and sugars. Dawes and Edwards (1966) identified methyl-substituted pyrazine in the volatile reaction products of a heated aqueous mixture of amino acids with D-fructose and suggested that the carbon atoms of pyrazines rose from sugar degradation. However, pyrazine compounds also occur in the reaction mixtures of ammonia and reducing sugars (Brandes and Stoehr, 1896; Jezo and Luzak, 1966; van Praag *et al.*, 1968), and their reaction temperatures were not too high, usually at the boiling point of the mixture solution.

During the thermal degradation of proteins, no significant amount of NH₃ is released until a certain temperature is reached, *e.g.*, evolution of NH₃ from trypsin increases rapidly when the temperature reaches 190° C, becomes maximum about 230° C, and decreases thereafter (Kasarda and Black, 1968). In the case of soybeans, we assumed that the soybean proteins were the major source of NH₃ evolution during deep fat frying, and the NH₃ probably reacted with the available reducing sugars to form pyrazine compounds during deep fat drying. If this is the case, the NH₃ availability, which is temperature dependent, may be one of the decisive factors for the formation of pyrazine compounds during soybean food preparation. The fact that none of the pyrazine compounds have been found in soy milk volatiles is related to the processing temperature (about 100° C) which is not high enough for NH₃ to arise from the soy proteins in the milk.

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